From structure topology to chemical composition. XX. Titanium silicates: the crystal structure of hejtmanite, Ba2Mn4Ti2(Si2O7)(2)O-2(OH)(2)F-2, a Group-II TS-block mineral

From structure topology to chemical composition. XX. Titanium silicates: the crystal structure of hejtmanite, $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$, a Group-II TS-block mineral

E. Sokolova[1]*, F. Cámara[2,3], F.C. Hawthorne[1], and L.A. Pautov[4]

[1] Department of Geological Sciences, University of Manitoba, Winnipeg, MB, R3T 2N2, Canada

[2] Dipartimento di Scienze della Terra, Università di Torino, I-10125, Torino, Italy

[3] CrisDi - Interdepartmental Center for Crystallography, via Giuria 7, 10126, Torino, Italy

[4] A.E. Fersman Mineralogical Museum, Russian Academy of Sciences, Leninskii Prospekt 18-2, Moscow 117071, Russia

* E-mail: elena_sokolova@umanitoba.ca

Mineralogical Society

This is a 'preproof' accepted article for Mineralogical Magazine.
This version may be subject to change during the production process.
10.1180/minmag.2016.080.026

Abstract

The crystal structure of hejtmanite, $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$, from Mbolve Hill, Mkushi River area, Central Province, Zambia (holotype material) has been refined on a twinned crystal to R_1 = 1.88% on the basis of 4539 [$|F| > 4\sigma|F|$]. Hejtmanite is triclinic, $C\bar{1}$, a = 10.716(2), b = 13.795(3), c = 11.778(2) Å, α = 90.07(3), β = 112.24(3), γ = 90.03(3)°, V = 1612(2) Å^3. Chemical analysis (electron microprobe) gives: Ta_2O_5 0.09, Nb_2O_5 1.27, ZrO_2 0.65, TiO_2 14.35, SiO_2 23.13, BaO 26.68, SrO 0.19; FeO 11.28, MnO 15.12, Cs_2O 0.05, K_2O 0.33, F 3.82, $H_2O_{calc.}$ 1.63, O=F –1.61, total 97.10 wt.%, where the H_2O content was calculated from the crystal-structure refinement, with (OH + F) = 4 a.p.f.u. The empirical formula, calculated on the basis of 20 (O + F) anions, is of the form $A^P{}_2M^O{}_4M^H{}_2(Si_2O_7)_2(X^O)_4(X^P)_2$, Z = 4: $(Ba_{1.82}K_{0.07}Sr_{0.02})_{\Sigma 1.91}(Mn_{2.33}Fe^{2+}{}_{1.65}Zr_{0.04}Mg_{0.03})_{\Sigma 3.95}(Ti_{1.88}Nb_{0.10}Zr_{0.02})_{\Sigma 2}(Si_{2.02}O_7)_2O_2[(OH)_{1.89}F_{0.11}]_{\Sigma 2}F_2$. The crystal structure is a combination of a TS (Titanium Silicate) block and an **I** (intermediate) block. The TS block consists of HOH sheets (H-heteropolyhedral, O-octahedral). The topology of the TS block is as in Group-II TS-block minerals: Ti (+ Nb) = 2 a.p.f.u. per $(Si_2O_7)_2$ [as defined by Sokolova (2006)]. In the O sheet, five $^{[6]}M^O$ sites are occupied mainly by Mn, less Fe^{2+} and minor Zr and Mg, with $<M^O–\varphi>$ = 2.198 Å (φ = O,OH), ideally giving Mn_4 a.p.f.u. In the H sheet, two $^{[6]}M^H$ sites are occupied mainly by Ti, with $<M^H–\varphi>$ = 1.962 Å (φ = O,F), ideally giving Ti_2 a.p.f.u.; four $^{[4]}Si$ sites are occupied by Si, with <Si–O> = 1.625 Å. The M^H octahedra and Si_2O_7 groups constitute the H sheet. The two $^{[12]}$Ba-dominant $A^P(1,2)$ sites, with $<A^P\text{-}\varphi>$ = 2.984 Å (φ = O, F), ideally give Ba_2 a.p.f.u. Two $X^O{}_M(1,2)$ and two $X^O{}_A(1,2)$ sites are occupied by O atoms and OH groups with minor F, respectively, ideally giving $(X^O)_4 = (X^O{}_M)_2 + (X^O{}_A)_2 = O_2(OH)_2$ p.f.u. Two $X^P{}_M(1,2)$ sites are occupied by F, giving F_2 a.p.f.u. TS blocks link via a layer of Ba atoms which constitute the **I** block. Simplified and endmember formulae of hejtmanite are $Ba_2(Mn,Fe^{2+})_4Ti_2(Si_2O_7)_2O_2(OH,F)_2F_2$ and $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$, Z = 4. Hejtmanite is a Mn-analogue of bafertisite, $Ba_2Fe^{2+}{}_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$.

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10.1180/minmag.2016.080.026

Keywords: hejtmanite, holotype, electron microprobe, single-crystal X-ray diffraction, crystal structure, chemical formula, TS block, Group II.

Introduction

Semenov and Zhang Peishan (1959) described bafertisite, $BaFe_2TiSi_2O_9$, Z = 2, as a new mineral from the Bayan Obo REE deposit, Inner Mongolia, China. The crystal structure of bafertisite from the Bayan Obo deposit was determined by (1) Guan *et al*. (1963) and (2) Peng Zhizhong and Shen Jinchuan (1963): [1] monoclinic, space group *Cm*, *a* = 10.60, *b* = 13.64, *c* = 12.47 Å, β = 119.5°, [2] monoclinic, space group $P2_1/m$, *a* = 10.98, *b* = 6.80, *c* = 5.36 Å, β = 94°. Based on the structure-refinement results, Guan *et al*. (1963) and Peng Zhizhong and Shen Jinchuan (1963) gave the chemical formula of bafertisite as follows: $BaFe_2Ti[Si_2O_7]O(OH)_2$, Z = 8 and 2, respectively. Vrána *et al*. (1992) described hejtmanite from Mbolve Hill, Mkushi River area, Central Province, Zambia, as a manganese-dominant analogue of bafertiste: monoclinic, diffraction symbol *C*/**, *a* = 10.698(4), *b* = 13.768(5), *c* = 11.748(4) Å, β = 112.27(2)°, V = 1601(2) Å^3, $D_{meas.}$ = 4.02 g/cm^3. Vrána *et al*. (1992) determined the chemical composition of hejtmanite by electron microprobe (Table 2) and by analogy with bafertisite (Semenov and Zhang Peishan, 1959; Guan *et al*., 1963; Peng Zhizhong and Shen Jinchuan, 1963), and gave simplified and endmember formulae $Ba(Mn,Fe)_2TiO(Si_2O_7)(OH,F)_2$ and $BaMn_2TiO(Si_2O_7)(OH,F)_2$, Z = 8. Pautov (private communication, 1989; *Mineraly*, 1996) reported the occurrence of a Mn-analogue of bafertisite in a rhodonite-tephroite-spessartine-quartz association from the Muzeinoe gorge, the Inyl'chek mountain ridge, Tyan-Shan, South-Eastern Kirgizia, and gave its empirical and general formulae, $(Ba_{0.96}Na_{0.03}Ca_{0.01}Cs_{0.002})_{\Sigma1}(Mn_{1.70}Fe^{2+}_{0.17}Mg_{0.05}Al_{0.08})_{\Sigma2}(Ti_{0.93}Sn_{0.07}Nb_{0.015})_{\Sigma1.01}(Si_{1.97}Al_{0.02})_{\Sigma1.99}O_7O_{2.09}(H_2O)_{0.25}$ and $BaMn_2TiO(Si_2O_7)(OH)_2$, respectively. All the crystals of the material from Inyl'chek were heavily twinned, and complicated the structure work. Sokolova *et al.* (1989) reported the unit cell for the Mn-analogue of bafertisite from the Inyl'chek mountain ridge, $BaMn_2TiO(Si_2O_7)(OH)_2$: triclinic, space groups *P*1 or $P\bar{1}$, *a* = 10.767(7), *b* = 13.858(9), *c* = 32.99(6) Å, α = 90.3(1), β = 94.6(1), γ = 89.96(5)°, V = 4906(2) Å^3, Z =24, and the structure model for the monoclinic subcell: space group *Pm*, *a* = 5.374(3), *b* = 6.911(3), *c* = 32.82(1) Å, β = 94.62(4)°, V = 1214(2) Å^3, *R* = 19.89%. They showed that the general topology of the structure of

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the Mn-analogue of bafertisite from the Inyl'chek mountain ridge is identical to that of bafertisite (Guan *et al*., 1963). Rastsvetaeva *et al.* (1991) collected new X-ray diffraction data using the crystal of the Mn-analogue of bafertisite from the Inyl'chek mountain ridge previously studied by Sokolova *et al.* (1989). They considered the crystal in question to be an intergrowth of two monoclinic phases of the composition $BaMn_2TiO(Si_2O_7)(OH)_2$: (1) space group $P2_1/m$, a = 5.361, b = 6.908, c = 12.556 Å, β = 119.8°, V = 403 Å^3, Z = 2, R = 6.8%, and (2) space group Cm, a = 10.723, b = 13.812, c = 12.563 Å, β = 119.9°, V = 1613 Å^3, Z = 8, R = 8.3%; both phases are isostructural with bafertisite [*cf*. $P2_1/m$ and Cm bafertisite structures of Peng Zhizhong and Shen Jinchuan (1963) and Guan *et al*. (1963), respectively]. However, both structures of Rastsvetaeva *et al*. (1991) have Si-O distances that are too short: (1) space group $P2_1/m$: 1.54 Å, and (2) space group Cm: 1.49 Å. These distances imply significant errors in both structures. The problems with the crystal structure of hejtmanite arise from the poor quality of its crystals, which is related to the extensive twinning [*cf*. bafertisite, Cámara *et al*. (2015*b*)] and possible intergrowths with other phases, a common problem with TS-block minerals. Based on the structure work of Rastsvetaeva *et al*. (1991), Sokolova (2006) and Sokolova and Cámara (2013) considered hejtmanite a TS-block mineral with two modifications: hejtmanite-C (space group Cm) and hejtmanite-P (space group $P2_1/m$).

The TS (Titanium Silicate) block is the main structural unit in the fast-growing family of forty minerals: thirty-four minerals are listed in Sokolova and Cámara (2013), and information on six minerals, kolskyite, emmerichite, saamite, betalomonosovite, bobshannonite and fogoite-(Y) can be found in Cámara *et al*. (2013), Aksenov *et al*. (2014), Cámara *et al*. (2014*a*), Sokolova *et al*. (2015*a*), Sokolova *et al*. (2015*b*) and Cámara *et al*. (2015*a*), respectively [*cf.* twenty-four minerals (Sokolova, 2006)]. The TS block consists of a central trioctahedral (O) sheet and two adjacent heteropolyhedral (H) sheets of [5-7]-coordinated polyhedra and Si_2O_7 groups. The TS block is characterized by a planar cell based on minimal lengths of translational vectors, t_1 ~ 5.5 and t_2 ~ 7 Å, and $\mathbf{t_1} \wedge \mathbf{t_2} \approx 90°$. The general formula of the TS block is $A^P{}_2B^P{}_2M^H{}_2M^O{}_4(Si_2O_7)_2X_{4+n}$,

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where M^H_2 and M^O_4 = cations of the H and O sheets; M^H = Ti, Nb, Zr, Mn, Ca + REE, Ca; M^O = Ti, Zr, Nb, Fe^{2+}, Fe^{3+}, Mg, Mn, Ca, Na; A^P and B^P = cations at the peripheral (*P*) sites = Na, Ca + REE, Ca, Ba, Sr, K; X = anions, O, OH, F, and H_2O groups; $X_{4+n} = X^O_4 + X^P_n$, n = 0, 1, 1.5, 2, 4, where X^O_4 = anions of the O sheet which do not coordinate Si atoms, X^P_n = anions at the periphery of the TS block; X = O, OH, F, H_2O (Sokolova and Cámara, 2013). Sokolova (2006) developed general structural principles for the TS-block minerals. There are three topologically distinct TS blocks based on three types of linkage of H and O sheets. In the crystal structures of TS-block minerals, TS blocks either link directly or alternate with intermediate (**I**) blocks. The **I** block consists of alkali and alkaline-earth cations, oxyanions (PO_4), (SO_4) and (CO_3), and H_2O groups. Sokolova (2006) divided TS-block structures into four Groups, based on the topology and stereochemistry of the TS block. Each group of structures has a different linkage, content and stereochemistry of Ti (+ Nb + Zr + Fe^{3+} + Mg + Mn) per $(Si_2O_7)_2$. In Group I, Ti (+ Nb + Zr) = 1 a.p.f.u. (atoms per formula unit); in Group II, Ti (+ Nb) = 2 a.p.f.u.; in Group III, Ti (+ Nb + Mg + Fe^{3+}) = 3 a.p.f.u.; in Group IV, Ti (+ Mg + Mn) = 4 a.p.f.u. In a TS-block structure, four types of self-linkage between adjacent TS blocks occur.

Sokolova and Cámara (2013) introduced the concept of *basic* and *derivative structures* for TS-block minerals. A *basic structure* has the following four characteristics: (1) There is only one type of TS block; (2) The two H sheets of the TS block are identical; (3) There is only one type of **I** block or it is absent; (4) There is only one type of self-linkage of TS blocks. *Basic structures* obey the general structural principles laid out by Sokolova (2006). A *derivative structure* has one or more of the three following characteristics: (1) There is more than one type of TS block; (2) There is more than one type of **I** block; (3) There is more than one type of self-linkage of TS blocks. A *derivative structure* is related to two or more *basic structures* of the same Group: it can be derived by adding these structures via sharing the central O sheet of the TS blocks of adjacent structural fragments which represent *basic structures*. There are thirty-five basic TS-block structures and five derivative TS-block structures.

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Following our continued interest in TS-block minerals, we felt strongly that the crystal structure of hejtmanite must be solved and refined on the holotype material of Vrána *et al*. (1992). We studied hejtmanite from (1) Mbolve Hill, Mkushi River area, Central Province, Zambia (holotype material from the collection of Leonid A. Pautov, given to Leonid by Stanislav Vrána), and (2) from the Muzeinoe gorge, the Inyl'chek mountain ridge, Tyan-Shan, South-Eastern Kirgizia. The current paper reports the crystal structure and structural formula of hejtmanite, $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$, a TS-block mineral of Group II where Ti (+ Nb) = 2 a.p.f.u. per $(Si_2O_7)_2$ (Table 1).

Chemical composition

Crystals of hejtmanite were analyzed with a Cameca SX-100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 10 μm. The following standards were used: Si: diopside; Ta: $Mn(Ta_{1.70}Nb_{0.30})O_6$; Nb, Ba: $Ba_2NaNb_5O_{15}$; Zr: zircon; Ti: titanite; Fe: fayalite; Mn: spessartine; Mg: forsterite; Sn: cassiterite; Sr: $SrTiO_3$; Cs: pollucite; K: orthoclase; F: fluorite. The elements Na, Al, Zn, Ca, Pb, Rb and Cl were sought but not detected. The data were reduced and corrected by the *PAP* method of Pouchou and Pichoir (1985). The H_2O (presence of OH groups confirmed by IR spectroscopy, Vrána *et al*., 1992) was calculated from the results of the crystal-structure analysis on the basis that F + OH = 4 a.p.f.u. Table 2 gives the chemical composition of hejtmanite from Zambia (holotype material) compared with its original chemical analysis (Vrána *et al*., 1992) and hejtmanite from Inyl'chek, Kirgizia. The empirical formula was calculated on the basis of 20 (O + F) anions and is of the form $A^P{}_2M^O{}_4M^H{}_2(Si_2O_7)_2(X^O)_4(X^P)_2$, Z =4: For hejtmanite from Zambia (holotype), it is $(Ba_{1.82}K_{0.07}Sr_{0.02})_{\Sigma 1.91}$ $(Mn_{2.33}Fe^{2+}{}_{1.65}Zr_{0.04}Mg_{0.03})_{\Sigma 3.95}(Ti_{1.88}Nb_{0.10}Zr_{0.02})_{\Sigma 2}(Si_{2.02}O_7)_2O_2\,[(OH)_{1.89}F_{0.11}]_{\Sigma 2}\,F_2$, $D_{calc.}$ = 4.189 g/cm^3 and is in accord with $D_{meas.}$ = 4.02 g/cm^3 (Vrána *et al*., 1992). For hejtmanite from Inyl'chek, Kirgizia, it is $Ba_{1.92}(Mn_{3.62}Fe^{2+}{}_{0.25}Mg_{0.08}Zr_{0.02})_{\Sigma 3.97}(Ti_{1.59}Sn_{0.42})_{\Sigma 2.01}(Si_{2.02}O_7)_2O_2$

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$[(OH)_{1.93}F_{0.07}]_{\Sigma 2}F_2$, $D_{calc.}$ = 4.189 g/cm^3. Hejtmanite from Inyl'chek, Kirgizia, is characterized by very high MnO, significant SnO_2, lower TiO_2 and lack of Nb_2O_5: 23.91, 5.95, 11.82 and 0 wt.%, respectively, *cf*. 14.12, 0, 14.35 and 1.27 wt.%, respectively (hejtmanite from Zambia, this work) (Table 2). By analogy with Sn-rich astrophyllite where Sn^{4+} constitutes ~ 31% of the Ti-dominant *D* site in the H sheet of the HOH block (Cámara *et al*., 2010), we assigned all Sn^{4+} to the Ti-dominant M^H site in the H sheet of the TS block (Table 2): $(Ti_{1.59}Sn_{0.42})_{\Sigma 2.01}$ a.p.f.u. Simplified and endmember formulae of hejtmanite are $Ba_2(Mn,Fe^{2+})_4Ti_2(Si_2O_7)_2O_2(OH,F)_2F_2$ and $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$, Z =4.

Crystal structure

Data collection and structure refinement

Single-crystal X-ray data for hejtmanite from Zambia were collected using a Bruker APEX II ULTRA three-circle diffractometer with a rotating-anode generator (Mo*K*α), multilayer optics and an APEX II 4K CCD detector. The intensities of 9468 reflections with –15 < *h* < 15, –19 < *k* < 19, –16 < *l* < 16 were measured to 60.28° 2θ using 16 s per 0.3° frame. Unit-cell dimensions were determined by least-squares refinement of 9989 reflections with $I > 10\sigma I$, and are given in Table 3, together with other miscellaneous information on data collection and structure refinement. An absorption correction was done using the SADABS program (Sheldrick, 2008). The unit-cell dimensions of hejtmanite (this work) are in good agreement with those of Vrána *et al*. (1992) (Table 3). All calculations were done with the Bruker SHELXTL version 5.1 system of programs (Sheldrick, 2008). The crystal structure was refined in space group $C\bar{1}$ using the atom coordinates of bafertisite (Cámara *et al*., 2015) and refined to R_1 = 1.88% on a twinned crystal with two components related by the twin matrix [100 0$\bar{1}$0 001] and a twin ratio of 0.526(1):0.474(1). The (Niggli) reduced unit cell is: *a* = 8.732(2), *b* = 8.736(2), *c* = 11.778(2) Å, α = 103.37(3), β = 103.48(3), γ = 104.32(3)°, *V* = 806(1) Å^3, $P\bar{1}$, *Z* = 2. The $P\bar{1}$ unit cell can be derived from the $C\bar{1}$ unit cell via the transformation matrix [-½-½0 -½½0 00-1]. We chose the

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unconventional space group $C\bar{1}$ for consistency of orientation with all other thirty-nine TS-block structures characterized by the planar cell based on minimal lengths of translational vectors, t_1 ~ 5.5 and t_2 ~ 7 Å, and $\mathbf{t_1} \wedge \mathbf{t_2} \approx 90°$, and specifically with bafertisite, the Fe^{2+}-analogue of hejtmanite. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson, 1992). In the crystal structure of bafertisite, there are 3 groups of cation sites: M^O sites of the O sheet, M^H and *Si* sites of the H sheet, and peripheral A^P sites which occur in the **I** block; site labeling is in accord with Sokolova (2006). Site-scattering values were refined for the M^O(1–5) sites with the scattering curve of Mn, M^H(1,2) sites (scattering curve of Ti) and A^P(1,2) sites (scattering curve of Ba). For the H(1,2) atoms, the D (donor)–H distances were softly constrained to 0.98 Å. Final atom coordinates and anisotropic displacement parameters for hejtmanite are listed in Table 4, selected interatomic distances and angles are given in Table 5, refined site-scattering values and assigned site-populations for selected cation and anion sites are given in Table 6, bond-valence values for selected anions in Table 7 and details of hydrogen bonding in Table 8. A table of structure factors and CIF for hejtmanite have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat.html.

Topology of the structure

Hejtmanite is a TS-block mineral of Group II, Ti (+ Nb) = 2 a.p.f.u. per $(Si_2O_7)_2$ (Sokolova, 2006). The crystal structure of hejtmanite is a combination of a TS block and an **I** block (Fig. 1*a*). The TS block consists of HOH sheets. In the O sheet, there are five Mn-dominant $^{[6]}M^O$(1–4) sites, with $<M^O–\varphi>$ = 2.198 Å (φ = O, OH) (Tables 5, 6, Fig. 1*b*). Five M^O sites ideally give Mn_4 a.p.f.u. (Table 6). In the H sheet, the two $^{[6]}M^H$(1,2) sites are occupied mainly by Ti and minor Nb and Zr, ideally giving Ti_2 a.p.f.u., with $<M^H–\varphi>$ = 1.962 Å (φ = O, F) and four $^{[4]}Si$ sites are occupied solely by Si, with <Si–O> = 1.625 Å (Tables 5, 6). The M^H octahedra and Si_2O_7 groups constitute the H sheet (Fig. 1*c*). Two H sheets and the central O sheet link via common vertices

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of M^H octahedra and Si_2O_7 groups with M^O octahedra to form the TS block. In Group II, the TS block exhibits linkage 2 where the Si_2O_7 groups of two H sheets link to M^O octahedra adjacent along $\mathbf{t}_2$ (|| **b** where $b = 2t_2$) in the O sheet (Fig. 1*a*) as defined by Sokolova (2006). There are two $^{[12]}$Ba-dominant $A^P(1,2)$ sites, with $\langle A^P(1)–\varphi\rangle$ = 2.934 Å and $\langle A^P(2)–\varphi\rangle$ = 3.034 Å (φ = O, F). The two A^P sites ideally give Ba_2 a.p.f.u. (Table 6). In the crystal structure of hejtmanite, TS blocks link via a layer of Ba atoms which constitute the **I** block (Fig. 1*a*). The topology of the hejtmanite structure is identical to that of bafertisite (Cámara *et al.*, 2015).

Anion considerations

The O(1–14) atoms coordinate Si atoms of Si_2O_7 groups, giving $(Si_2O_7)_2$ p.f.u. Two $X^O_M(1,2)$ anions are bonded to one M^H (Ti) cation and three M^O (Mn) cations, receive 1.84 and 1.85 vu (valence units) and hence they are O atoms, giving O_2 a.p.f.u. (Tables 5–7). Two $X^P_M(1,2)$ anions are bonded to one M^H (Ti) cation and three A^P (Ba) cations (Fig. 1*d*), they receive 0.84 and 0.82 vu (Table 7). We conclude that the $X^P_M(1,2)$ anions are monovalent. The two X^P_M sites are coordinated by four cations and hence there is no space to accommodate the H atom of an OH group and a hydrogen bond at those sites. Therefore we assign F to the $X^P_M(1,2)$ sites, and they give F_2 a.p.f.u. (Table 6). Two $X^O_A(1,2)$ anions are bonded to three M^O (Mn) cations, with incident valence sums of 1.18 and 1.22 vu (Table 7), hence they are monovalent anions. Chemical analysis gives 2.11 F a.p.f.u. for hejtmanite (Table 2) and we assign 1.89 OH + [2.11 – 2.00$(X^P_M)_2$ =] 0.11 F to the $X^O_A(1,2)$ sites, ideally $(OH)_2$ a.p.f.u. (Table 6). The H(1,2) atoms are involved in weak hydrogen bonding with O atoms that belong to the H sheets (Table 8).

Endmember formula

We write the endmember formula of hejtmanite as the sum of the groups of cation and anion sites: Ba_2 (A^P_2) + Mn_4 (M^O_4) + Ti_2 (M^H_2) + $(Si_2O_7)_2$ + O_2 [$(X^O_M)_2$] + $(OH)_2$ [$(X^O_A)_2$] + F_2 [$(X^P_M)_2$] = $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$, Z =4.

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Basic TS-block structure

In the crystal structure of hejtmanite, (1) there is only one type of TS block of composition $[Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2]^{4-}$; (2) the two H sheets of the TS block are identical; (3) there is only one type of **I** block of composition $[Ba_2]^{4+}$; and (4) there is only one type of self-linkage of TS blocks, via a layer of Ba atoms in the of **I** block. Points (1)–(4) are in accord with the definition of a basic structure by Sokolova and Cámara (2013). The crystal structure of hejtmanite is of the B2(GII) structure type in accord with Sokolova and Cámara (2013).

On F in the Group-II TS-block structures

Ideal structural formulae for Group-II minerals hejtmanite and bafertisite (the bafertisite structure type, B2); bobshannonite, perraultite and jinshajiangite (the perraultite structure type, B1), cámaraite (the D1 cámaraite structure type related to the bafertisite and perraultite structure types), yoshimuraite (B3) and bussenite (B4) are presented in Table 1. All minerals have basic structures except for cámaraite. In perraultite, jinshajiangite and bobshannonite, TS blocks connect via M^H- X^P_M-M^H bridges as in the astrophyllite-group minerals (Cámara *et al.*, 2010) and related nafertisite, $Na_3Fe^{2+}_{10}Ti_2(Si_6O_{17})_2O_2(OH)_6F(H_2O)_2$ (Cámara *et al.*, 2014*b*). The composition of an X^P_M anion correlates with the composition of the M^H cations: where M^H sites are locally occupied by Nb (as in bobshannonite), the bridging anion is an O atom; where M^H sites are locally occupied by Ti (as in perraultite and jinshajiangite), the bridging anion is a F atom (Table 1). A similar phenomenon was noted for astrophyllite-group minerals (*cf*. niobophyllite, Cámara *et al.*, 2010). In most astrophyllite-group minerals, the X^P_M anion is coordinated by six cations: two Ti or Nb (at the M^H site), two K (at the *A* site) and two Na (at the *B* site) and an OH group cannot/does not occur at the X^P_M site as there is no room to accommodate an H atom and a hydrogen bond; where there is a vacancy at the *A* or *B* sites, OH groups occur at the X^P_M site (Sokolova, 2012). In bafertisite and hejtmanite, TS blocks

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connect via a layer of Ba atoms in the **I** block. F (X^{P}_{M} site) atoms are apical anions of the M^{H} (=Ti) cations and they are coordinated by four cations: Ti (M^{H} site) and three Ba [A^{P}(1,2) sites]. In bafertisite and hejtmanite, an OH group cannot occur at the X^{P}_{M} site as there is no room to accommodate an H atom and a hydrogen bond. Hence F atoms and OH groups are ordered at the X^{P}_{M} and X^{O}_{A} sites, respectively.

Hejtmanite is related to cámaraite, ideally $NaBa_3Fe^{2+}_8Ti_4(Si_2O_7)_4O_4(OH)_4F_3$. The derivative structure of cámaraite has one type of TS block, two types of **I** block, and TS blocks link to each other in two different ways. The structure of cámaraite can be built of structural fragments of minerals of the same group, jinshajiangite and bafertisite. The *bafertisite* component of the cámaraite structure is topologically identical to the hejtmanite structure. The general and ideal structural formulae of cámaraite are written as sums of the corresponding formulae of bafertisite and jinshajiangite (Table 1).

Summary

(1) Hejtmanite, ideally $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$, is a Group-II TS-block mineral (Ti + Nb = 2 a.p.f.u.) in accord with Sokolova (2006). The crystal structure of bafertisite [a = 10.716(2), b = 13.795(3), c = 11.778(2) Å, α = 90.07(3), β = 112.24(3), γ = 90.03(3)°, V = 1612(2) Å^3, space group $C\bar{1}$] is of basic type [B2(GII)] and is an alternation of TS and **I** blocks of the composition $[Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2]^{4-}$ and $[Ba_2]^{4+}$, respectively. The crystal structure of hejtmanite is of the same topology as that of baferisite, $Ba_2Fe^{2+}_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$.

(2) In the crystal structure of hejtmanite, OH groups and F atoms are ordered at the X^{O}_{A} sites in the O sheet and X^{P}_{M} sites on the periphery of the TS block.

(3) The endmember formula of hejtmanite is of the form $A^{P}_2M^{O}_4M^{H}_2(Si_2O_7)_2(X^{O})_4(X^{P})_2$: $Ba_2Mn_4Ti_2(Si_2O_7)_2O_2(OH)_2F_2$, Z =4 where Ba_2 $A^{P}_2 = Ba_2$, $M^{O}_4 = Mn_4$, $M^{H}_2 = Ti_2$, $(X^{O})_4 = (X^{O}_{M})_2 + (X^{O}_{A})_2 = O_2(OH)_2$, $(X^{P}_{M})_2 = F_2$.

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Acknowledgements

We thank Mark Cooper for collecting single-crystal X-ray data for hejtmanite. LAP acknowledges financial support by the grant 12-05-00911-a from the Russian Foundation for Basic Research; FC acknowledges financial support by the grant Ricerca Locale 2014, Università di Torino; FC and ES were supported by a Canada Research Chair in Crystallography and Mineralogy and by a Discovery grant from the Natural Sciences and Engineering Research Council of Canada and by Innovation Grants from the Canada Foundation for Innovation to FCH.

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Figure captions

Fig. 1. A general view of the crystal structure of hejtmanite which consists of TS and **I** blocks (*a*) and the details of the structure: the close-packed O sheet of Mn-dominant M^{O} octahedra (*b*), the H sheet of Ti-dominant M^{H} octahedra and Si_2O_7 groups (*c*), the F atom at the X^{P}_{M} site coordinated by the four cations (*d*). SiO_4 tetrahedra are orange, Ti-dominant and Mn-dominant octahedra are yellow and magenta, respectively; Ba atoms at the A^{P} sites in the **I** block are shown as raspberry spheres; O and H atoms of OH groups at the X^{O}_{A} sites are shown as turquoise and small white spheres; F atoms at the X^{P}_{M} sites are shown as yellow spheres. Unit cell is shown by thin black lines.

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TABLE 1. Ideal structural formulae* and unit-cell parameters for Group-II TS-block minerals, Ti + Nb = 2 a.p.f.u. per $(Si_2O_7)_2$.

Mineral	Formula									*a* (Å)	*b* (Å)	*c* (Å)	Sp. gr.	*Z*	Ref.
Structure type**	A^P_{1-2}	B^P_{0-2}	$\mathbf{M^H_2}$	$\mathbf{M^O_4}$	$\mathbf{(Si_2O_7)_2}$		$\mathbf{(X^O_M)_2}$	$\mathbf{(X^O_A)_2}$	$(X^P_M)_{0-2}$	α (°)	β (°)	γ (°)			
hejtmanite B2(GII)	Ba_2		$\mathbf{Ti_2}$	$\mathbf{Mn_4}$	$\mathbf{(Si_2O_7)_2}$		$\mathbf{O_2}$	$\mathbf{(OH)_2}$	F_2	10.716 90.07	13.795 112.24	11.778 90.03	$C\bar{1}$	4	(1)
bafertisite B2(GII)	Ba_2		$\mathbf{Ti_2}$	$\mathbf{Fe^{2+}_4}$	$\mathbf{(Si_2O_7)_2}$		$\mathbf{O_2}$	$\mathbf{(OH)_2}$	F_2	10.677 90.11	13.767 112.28	11.737 90.02	$C\bar{1}$	4	(2)
cámaraite[1] D1(GII)	Ba_3	Na	$\mathbf{Ti_4}$	$\mathbf{Fe^{2+}_8}$	$\mathbf{(Si_2O_7)_4}$		$\mathbf{O_4}$	$\mathbf{(OH)_4}$	F_3	10.6965 99.345	13.7861 92.315	21.478 89.993	$C\bar{1}$	4	(3)
jinshajiangite B1(GII)	Ba	Na	$\mathbf{Ti_2}$	$\mathbf{Fe^{2+}_4}$	$\mathbf{(Si_2O_7)_2}$		$\mathbf{O_2}$	$\mathbf{(OH)_2}$	F	10.7059 90.008	13.7992 94.972	20.760 89.984	$C\bar{1}$	8	(4)
perraultite B1(GII)	Ba	Na	$\mathbf{Ti_2}$	$\mathbf{Mn_4}$	$\mathbf{(Si_2O_7)_2}$		$\mathbf{O_2}$	$\mathbf{(OH)_2}$	F	10.731 90	13.841 95.06	20.845 90	$C2$	8	(5)
bobshannonite[1] B1(GII)	Ba K	Na_2	$\mathbf{(Nb,Ti)_4}$	$\mathbf{(Mn,Na)_8}$	$\mathbf{(Si_2O_7)_4}$		$\mathbf{O_4}$	$\mathbf{(OH)_4}$	$(O,F)_2$	10.839 89.99	13.912 95.02	20.98 89.998	$C\bar{1}$	4	(6)
yoshimuraite[2] B3(GII)	Ba_2	Ba_2	$\mathbf{^{[5]}Ti_2}$	$\mathbf{Mn_4}$	$\mathbf{(Si_2O_7)_2}$	$(PO_4)_2$	$\mathbf{O_2}$	$\mathbf{(OH)_2}$		5.386 95.50	6.999 93.62	14.748 89.98	$P\bar{1}$	2	(7)
bussenite[3] B4(GII)	$(Na□)_2$	Ba_2	Ba_2	$\mathbf{Ti_2}$	$\mathbf{(M^{2+}Na)_2}$	$\mathbf{(Si_2O_7)_2}$	$(CO_3)_2$	$\mathbf{O_2}$	$\mathbf{(OH)_2}$	$(H_2O)_2$	F_2	5.399 102.44	7.016 93.18	16.254 90.10	$P\bar{1}$	2	(8)

* The general structural formula of the TS block is $A^P_2B^P_2\mathbf{M^H_2M^O_4(Si_2O_7)_2X_{4+n}}$, where M^H_2 and M^O_4 = cations of the H and O sheets; A^P and B^P = cations at the peripheral (*P*) sites; X = anions; $X_{4+n} = X^O_4 + X^P_n$, n = 0, 1, 1.5, 2, 4 (Sokolova and Cámara, 2013). $X^O_4 = (X^O_M)_2 + (X^O_A)_2$: X^O_M = anions at common vertices of $3M^O$ and M^H polyhedra and X^O_A = anions at common vertices of $3M^O$ and A^P polyhedra (where $A^P–X^O_A < 3$ Å); X^P_M = apical anions of M^H cations at the periphery of the TS block. The stoichiometry of the core part of the TS block, $\mathbf{M^H_2M^O_4(Si_2O_7)_2X^O_4}$, is invariant in all structures (shown in bold). In Group II, A^P and B^P cations, plus $(PO_4)_2$ (in yoshimuraite) and $(Na□)_2(CO_3)_2F_2$ (in bussenite) constitute the **I** block.

** Bn(GII) and Dn(GII) denote B for basic and D for derivative structures of Group II (Sokolova and Cámara, 2013).

For yoshimuraite and bussenite, ideal structural formulae are from Sokolova (2006). Surkhobite (Rastsvetaeva *et al.*, 2008) is not listed here as there are problems with its crystal structure.

[1] the formulae for cámaraite and bobshannonite are per double minimal cell based on $2t_1$ and $2t_2$ translations $[(Si_2O_7)_4]$;

[2] there are misprints in McDonald *et al.* (2000): $\alpha = 89.98$, $\gamma = 95.50^o$;

[3] $M^{2+} = Fe^{2+}$, Mn;

References (the most recent reference on the structure): (1) this work; (2) Cámara *et al*. (2015*b*); (3) Cámara *et al*. (2009); (4) Cámara *et al.* (in preparation) and Sokolova *et al*. (2009); (5) Yamnova *et al.* (1998); (6) Sokolova *et al*. (2015*b*); (7) McDonald *et al.* (2000); (8) Zhou *et al.* (2002).

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TABLE 2. Chemical composition and unit formula* for hejtmanite.

Component	wt.%				Formula unit (a.p.f.u.)		
	← Zambia (holotype) →		Inyl'chek, Kirgizia		← Zambia (holotype) →		Inyl'chek, Kirgizia
	This work	Vrána *et al*. (1992)	This work		This work	Vrána *et al*. (1992)	This work
Ta_2O_5	0.09	n.d.	n.d.	Si	4.04	4.11	4.03
Nb_2O_5	1.27	1.4	n.d.				
SnO_2	n.d.	n.d.	5.95	Mn	2.23	2.09	3.62
ZrO_2	0.65	n.d.	0.22	Fe^{2+}	1.65	1.65	0.25
TiO_2	14.35	13.27	11.82	Zr	0.04	0	0.02
SiO_2	23.13	23.52	22.53	Mg	0.03	0.03	0.08
Al_2O_3	n.d.	0.37	n.d.	Na	0	0.02	0
BaO	26.68	30.20	27.41	$\Sigma 4M^O$	3.95	3.79	3.97
SrO	0.19	n.d.	n.d.				
FeO	11.28	11.29	1.65	Ti	1.88	1.75	1.59
MnO	15.12	14.12	23.91	Sn	0	0	0.42
CaO	n.d.	n.d.	0.04	Nb	0.10	0.11	0
MgO	0.12	0.13	0.30	Zr	0.02	0	0
Cs_2O	0.05	n.d.	0.04	Al	0	0.08	0
K_2O	0.33	0.30	n.d.	$\Sigma 2M^H$	2.00	1.94	2.01
Na_2O	n.d.	0.06	n.d.				
H_2O**	1.63	1.86	1.62	Ba	1.82	2.07	1.92
F	3.82	3.30	3.66	Sr	0.02	0	0
Cl	n.d.	<0.1	n.d.	K	0.07	0.07	0
$-O=F_2,Cl_2$	1.61	1.39	1.54	$\Sigma 2A^P$	1.91	2.14	1.92
Total	97.10	98.43	97.61				
				Σcations	11.90	11.98	11.94
				F	2.11	1.82	2.07
				OH	1.89	2.18	1.93
				$\Sigma 2X^P_M + 2X^O_A$	4.00	4.00	4.00

n.d. – not detected;
* calculated on anion basis: O + F = 20 a.p.f.u.;
** calculated from structure solution and refinement (this work) and by crystallochemical calculations (Vrána *et al*., 1992): OH + F = 4 a.p.f.u.

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TABLE 3. Miscellaneous refinement data for hejtmanite.

	This work	Vrána *et al*. (1992)
a (Å)	10.716(2)	10.698(4)
b	13.795(3)	13.768(5)
c	11.778(2)	11.748(4)
α (°)	90.07(3)	90
β	112.24(3)	112.27(2)
γ	90.03(3)	90
V (Å^3)	1612(2)	1601(2)
Space group	$C\bar{1}$	*C**/* (diffraction symbol)
Z	4	4
Absorption coefficient (mm^{-1})	9.00	
F(000)	1885.8	
$D_{calc.}$ (g/cm^3)	4.189	4.29
Crystal size (mm)	0.004 x 0.025 x 0.040	
Second component*	0.474(1)	
Radiation/monochromator	MoKα/graphite	
2θ-range for data collection (°)	60.28	
R(int) (%)	1.32	
Reflections collected	9468	
Independent reflections	4748	
$F_o > 4\sigma F$	4539	
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$	
No. of refined parameters	308	
Final *R* indices (%)		
R_1 ($F_o > 4\sigma F$)	1.88	
R_1	2.05	
wR_2	5.11	
Goodness of fit on F^2	1.090	

*Second component of the crystal is related to the first component by the twin matrix [100 0$\bar{1}$0 001].

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TABLE 4. Atom coordinates and anisotropic displacement parameters (Å^2) for hejtmanite.

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
M^O(1)	0	0	0	0.0071(5)	0.0103(5)	0.0145(5)	–0.0002(4)	0.0048(4)	0.0008(4)	0.0104(3)
M^O(2)	0.24447(4)	0.12358(6)	–0.01128(4)	0.0082(2)	0.0102(2)	0.0121(2)	0.0003(4)	0.00394(15)	–0.0001(3)	0.01016(12)
M^O(3)	0.25626(4)	0.87317(6)	0.00822(4)	0.0087(2)	0.0104(2)	0.0114(2)	–0.0002(4)	0.00396(14)	0.0001(4)	0.01009(12)
M^O(4)	0.99575(5)	0.75166(3)	0.99334(5)	0.0084(5)	0.0123(4)	0.0164(5)	0.0036(3)	0.0026(3)	–0.0001(3)	0.0130(3)
M^O(5)	½	0	0	0.0064(5)	0.0193(6)	0.0255(7)	–0.0109(5)	0.0023(4)	0.0023(4)	0.0182(3)
M^H(1)	0.46397(5)	0.60457(4)	0.71450(5)	0.0039(2)	0.0085(3)	0.0059(2)	0.00001(17)	0.00229(17)	0.00015(17)	0.00598(16)
M^H(2)	0.53708(5)	0.85658(4)	0.28856(5)	0.0038(2)	0.0094(4)	0.0061(2)	0.00073(18)	0.00235(17)	0.00029(18)	0.00627(17)
Si(1)	0.28264(14)	0.01493(9)	0.24821(13)	0.0077(5)	0.0061(5)	0.0072(5)	–0.0002(4)	0.0018(4)	0.0010(4)	0.0073(3)
Si(2)	0.71633(14)	0.76433(9)	0.75030(13)	0.0064(5)	0.0085(5)	0.0069(5)	0.0004(4)	0.0031(4)	0.0003(4)	0.0071(2)
Si(3)	0.74114(14)	0.48385(9)	0.74999(13)	0.0069(5)	0.0066(5)	0.0069(5)	–0.0002(4)	0.0028(4)	–0.0004(4)	0.0067(2)
Si(4)	0.26032(14)	0.73678(9)	0.24969(13)	0.0085(5)	0.0077(5)	0.0073(5)	0.0008(4)	0.0029(4)	–0.0001(4)	0.0079(3)
A^P(1)	0.61130(2)	0.62440(2)	0.46823(1)	0.00851(8)	0.01261(9)	0.00841(8)	0.00013(16)	0.00315(6)	0.00035(16)	0.00986(5)
A^P(2)	0.38948(2)	0.87832(3)	0.53561(2)	0.00985(9)	0.03465(14)	0.01072(10)	–0.0004(2)	0.00416(7)	–0.0019(2)	0.01833(7)
O(1)	0.4168(3)	0.95191(19)	0.3214(2)	0.0104(11)	0.0170(13)	0.0123(12)	0.0018(10)	0.0052(9)	0.0042(10)	0.0130(5)
O(2)	0.6702(3)	0.5008(2)	0.3061(2)	0.0123(12)	0.0140(13)	0.0152(12)	–0.0008(11)	0.0102(10)	–0.0020(10)	0.0123(5)
O(3)	0.2192(4)	1.0000(3)	0.1006(3)	0.0085(14)	0.0152(15)	0.0039(15)	–0.0002(12)	–0.0001(11)	0.0003(11)	0.0099(7)
O(4)	0.6560(19)	0.87436(18)	0.72513(17)	0.0107(8)	0.0095(9)	0.0104(9)	0.0000(10)	0.0031(7)	–0.0011(10)	0.0105(4)
O(5)	0.6724(3)	0.7532(2)	0.3096(3)	0.0108(12)	0.0162(13)	0.0144(12)	0.0066(11)	0.0064(9)	0.0040(11)	0.0133(5)
O(6)	0.7838(4)	0.7504(2)	0.8986(4)	0.0099(14)	0.0083(14)	0.0107(16)	0.0006(12)	0.0048(12)	0.0006(11)	0.0094(7)
O(7)	0.5829(3)	0.69880(18)	0.6825(2)	0.0136(12)	0.0127(12)	0.0129(12)	–0.0016(10)	0.0069(9)	–0.0033(10)	0.0126(5)
O(8)	0.8186(3)	0.54787(18)	0.6829(3)	0.0112(12)	0.0147(13)	0.0145(12)	0.0000(11)	0.0062(9)	–0.0025(10)	0.0131(5)
O(9)	0.5806(2)	0.50058(19)	0.6939(2)	0.0077(11)	0.0156(13)	0.0137(12)	–0.0021(10)	0.0032(9)	0.0020(9)	0.0126(5)
O(10)	0.7975(4)	0.4969(3)	0.8984(3)	0.0106(15)	0.0143(15)	0.0053(15)	–0.0016(12)	0.0013(12)	0.0005(11)	0.0106(7)
O(11)	0.27786(19)	0.87280(19)	0.72202(17)	0.0112(8)	0.0086(9)	0.0118(9)	0.0007(10)	0.0049(7)	0.0002(10)	0.0104(4)
O(12)	0.2056(4)	0.7507(2)	0.101(4)	0.0096(15)	0.0090(14)	0.0103(16)	0.0003(12)	0.0051(12)	0.0001(11)	0.0092(7)
O(13)	0.4205(2)	0.75272(19)	0.3126(2)	0.0086(11)	0.0148(13)	0.0150(12)	0.0038(11)	0.0032(9)	–0.0000(10)	0.0132(5)
O(14)	0.3162(3)	0.69775(18)	0.6804(2)	0.0105(12)	0.0141(12)	0.01248	–0.0021(10)	0.0046(9)	0.0026(10)	0.0123(5)
X^O_M(1)	0.5347(2)	0.6161(3)	0.87959(19)	0.0094(9)	0.0158(14)	0.0096(9)	–0.0004(12)	0.0047(7)	–0.0016(11)	0.0113(5)
X^O_M(2)	0.4650(2)	0.8656(3)	0.12430(19)	0.0100(9)	0.0163(4)	0.0109(9)	–0.0020(12)	0.0040(7)	0.0000(12)	0.0123(5)
X^O_A(1)	–0.0432(2)	0.1243(3)	0.08664(18)	0.0135(9)	0.0118(10)	0.0106(9)	0.0008(15)	0.0043(7)	0.0013(16)	0.0120(4)
X^O_A(2)	0.45556(19)	0.1270(3)	0.07877(18)	0.0101(9)	0.0134(10)	0.0093(9)	–0.0002(16)	0.0031(7)	0.0003(16)	0.0111(4)
X^P_M(1)	0.61734(19)	0.40573(16)	0.47686(18)	0.0122(9)	0.0277(11)	0.0089(9)	–0.0012(7)	0.0040(7)	0.0004(8)	0.0162(4)
X^P_M(2)	0.61551(19)	0.85348(19)	0.48003(17)	0.0134(9)	0.0449(17)	0.0079(9)	0.0002(9)	0.0038(7)	0.0009(9)	0.0221(6)
H(1)	–0.003(3)	0.142(3)	0.1730(14)	0.01445*						
H(2)	0.494(3)	0.146(3)	0.1652(14)	0.01334*						

*U_{iso}

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TABLE 5. Selected interatomic distances (Å) and angles (°) in hejtmanite.

$M^{O}(1)–X^{O}_{A}(1)$	2.133(4)	x2	$M^{O}(2)–X^{O}_{A}(2)$	2.104(2)		$M^{O}(3)–X^{O}_{A}(1)$d	2.129(2)
$M^{O}(1)–O(3)$a	2.194(4)	x2	$M^{O}(2)–X^{O}_{M}(1)$b	2.128(2)		$M^{O}(3)–X^{O}_{M}(2)$	2.137(2)
$M^{O}(1)–X^{O}_{M}(1)$b	2.262(3)	x2	$M^{O}(2)–O(6)$b	2.170(4)		$M^{O}(3)–O(3)$	2.174(4)
$<M^{O}(1)–\varphi>$	2.196		$M^{O}(2)–O(10)$b	2.228(4)		$M^{O}(3)–O(12)$	2.192(4)
			$M^{O}(2)–O(3)$a	2.234(4)		$M^{O}(3)–O(12)$e	2.270(4)
			$M^{O}(2)–O(6)$c	2.275(4)		$M^{O}(3)–O(10)$f	2.284(4)
			$<M^{O}(2)–\varphi>$	2.190		$M^{O}(3)–\varphi>$	2.198
$M^{O}(4)–X^{O}_{A}(1)$c	2.107(4)		$M^{O}(5)–O(10)$b	2.044(4)	x2		
$M^{O}(4)–X^{O}_{A}(2)$g	2.118(4)		$M^{O}(5)–X^{O}_{A}(2)$	2.119(4)	x2		
$M^{O}(4)–O(6)$	2.118(4)		$M^{O}(5)–X^{O}_{M}(2)$a	2.479(3)	x2		
$M^{O}(4)–O(12)$h	2.123(4)		$<M^{O}(5)–\varphi>$	2.214			
$M^{O}(4)–X^{O}_{M}(2)$j	2.270(3)						
$M^{O}(4)–X^{O}_{M}(1)$i	2.458(3)						
$<M^{O}(4)–\varphi>$	2.199						
$M^{H}(1)–X^{O}_{M}(1)$	1.807(2)		$M^{H}(2)–X^{O}_{M}(2)$	1.796(2)		Si(1)–O(2)k	1.605(3)
$M^{H}(1)–O(7)$	1.954(3)		$M^{H}(2)–O(8)$j	1.961(3)		Si(1)–O(1)a	1.622(3)
$M^{H}(1)–O(14)$	1.960(3)		$M^{H}(2)–O(1)$	1.980(3)		Si(1)–O(3)a	1.622(4)
$M^{H}(1)–O(9)$	1.977(3)		$M^{H}(2)–O(5)$	1.982(3)		Si(1)–O(4)c	1.645(3)
$M^{H}(1)–O(2)$c	1.994(3)		$M^{H}(2)–O(13)$	1.990(3)		<Si(1)–O>	1.624
$M^{H}(1)–X^{P}_{M}(1)$c	2.091(5)		$M^{H}(2)–X^{P}_{M}(2)$	2.088(2)			
$<M^{H}(1)–\varphi>$	1.964		$<M^{H}(2)–\varphi>$	1.960			
Si(2)–O(5)j	1.617(3)		Si(3)–O(9)k	1.609(3)		Si(4)–O(13)	1.607(3)
Si(2)–O(7)	1.623(3)		Si(3)–O(8)r	1.610(3)		Si(4)–O(12)	1.630(4)
Si(2)–O(6)	1.629(4)		Si(3)–O(10)	1.628(4)		Si(4)–O(11)m	1.633(3)
Si(2)–O(4)	1.633(3)		Si(3)–O(11)l	1.645(3)		Si(4)–O(14)m	1.636(3)
<Si(2)–O>	1.626		<Si(3)–O>	1.623		<Si(4)–O>	1.627
$A^{P}(1)–X^{P}_{M}(2)$j	2.772(2)		$A^{P}(2)–X^{P}_{M}(1)$n	2.757(2)		Si(1)c–O(4)–Si(2)	136.6(1)
$A^{P}(1)–X^{P}_{M}(1)$c	2.792(2)		$A^{P}(2)–X^{P}_{M}(2)$l	2.759(2)		Si(3)n–O(11)–Si(4)n	136.4(1)
$A^{P}(1)–O(13)$	2.801(3)		$A^{P}(2)–O(1)$	2.836(3)		<Si–O–Si>	136.5
$A^{P}(1)–O(2)$	2.803(3)		$A^{P}(2)–O(14)$m	2.860(3)			
$A^{P}(1)–O(9)$c	2.804(3)		$A^{P}(2)–O(11)$	2.871(2)			
$A^{P}(1)–O(5)$	2.830(3)		$A^{P}(2)–O(4)$	2.884(2)			
$A^{P}(1)–O(7)$	2.844(3)		$A^{P}(2)–O(1)$o	3.158(3)			
$A^{P}(1)–O(8)$	2.864(3)		$A^{P}(2)–O(8)$n	3.170(3)			
$A^{P}(1)–X^{P}_{M}(1)$	3.018(2)		$A^{P}(2)–O(13)$	3.265(3)			
$A^{P}(1)–X^{P}_{M}(2)$	3.163(3)		$A^{P}(2)–O(7)$	3.274(3)			
$A^{P}(1)–O(5)$j	3.235(3)		$A^{P}(2)–O(14)$	3.279(3)			
$A^{P}(1)–O(9)$	3.280(3)		$A^{P}(2)–O(2)$n	3.300(3)			
$<A^{P}(1)–\varphi>$	2.934		$<A^{P}(2)–\varphi>$	3.034			

a: *x*, *y*–1, *z*; b: *x*–1/2, *y*–1/2, *z*–1; c: –*x*+1, –*y*+1, –*z*+1; d: –*x*, –*y*+1, –*z*; e: –*x*+1/2, –*y*+3/2, –*z*; f: *x*–1/2, *y*+1/2, *z*–1; g: *x*+1/2, *y*+1/2, *z*+1; h: *x*+1, *y*, *z*+1; i: –*x*+3/2, –*y*+3/2, –*z*+2; j: –*x*+3/2, –*y*+3/2, –*z*+1; k: *x*–1/2, *y*–1/2, *z*; l: *x*+1/2, *y*–1/2, *z*; m: –*x*+1/2, –*y*+3/2, –*z*+1; n: *x*–1/2, *y*+1/2, *z*; o: –*x*+1, –*y*+2, –*z*+1

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TABLE 6. Refined site-scattering values and assigned site-populations for hejtmanite.

Site *	Refined site-scattering (e.p.f.u.)	Assigned site-population (a.p.f.u.)	Calculated site-scattering (e.p.f.u.)	<X-φ>$_{obs.}$** (Å)	Ideal composition (a.p.f.u.)
		Cations			
M^{O}(1)	12.70(6)			2.196	$Mn_{0.5}$
M^{O}(2)	25.94(7)			2.190	Mn
M^{O}(3)	25.85(7)	2.23 Mn + 1.65 Fe^{2+} + 0.04 Zn + 0.03 Mg + 0.05 □		2.198	Mn
M^{O}(4)	26.05(10)			2.199	Mn
M^{O}(5)	12.96(6)			2.214	$Mn_{0.5}$
ΣM^{O}(1-5)	103.50	2.23 Mn + 1.65 Fe^{2+} + 0.04 Zn + 0.03 Mg + 0.05 □	100.61		Mn_4
M^{H}(1)	22.62(7)	1.88 Ti + 0.10 Nb + 0.02 Zr		1.964	Ti
M^{H}(2)	22.56(6)			1.960	Ti
ΣM^{H}(1,2)	45.18	1.88 Ti + 0.10 Nb + 0.02 Zr	46.26		Ti_2
$^{[12]}A^{P}$(1)	55.21(10)	0.93 Ba + 0.02 Sr + 0.05 □	52.84	2.934	Ba
$^{[12]}A^{P}$(2)	53.48(10)	0.89 Ba + 0.07 K + 0.04 □	51.17	3.034	Ba
ΣA^{P}(1,2)	108.69	1.82 Ba + 0.07 K + 0.02 Sr + 0.09 □	104.01		Ba_2
		Anions			
ΣX^{O}_{M}(1,2)		2.00 O			O_2
ΣX^{O}_{A}(1,2)		1.89 OH + 0.11 F			$(OH)_2$
ΣX^{P}_{M}(1,2)		2.00 F			F_2

* coordination number is given only for non-[6]-coordinated sites;
** X = cation, φ = O, OH, F;

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TABLE 7. Bond-valence values* for selected anions in hejtmanite.

Atom	$M^O(1)$	$M^O(2)$	$M^O(3)$	$M^O(4)$	$M^O(5)$	$M^H(1)$	$M^H(2)$	$A^P(1)$	$A^P(2)$	Σ
$X^O_M(1)$	0.28	0.39		0.17		1.00				1.84
$X^O_M(2)$			0.38	0.27	0.17		1.03			1.85
$^{[3]}X^O_A(1)$	0.38		0.39	0.41						1.18
$^{[3]}X^O_A(2)$		0.42		0.40	0.40					1.22
$X^P_M(1)$						0.34		0.18 0.13	0.19	0.84
$X^P_M(2)$						0.34		0.19 0.10	0.19	0.82

* Bond-valence parameters (vu) are from Brown (1981); bond-valence values calculated for M^O = Mn; M^H = Ti; A^P = Ba; coordination numbers are shown for non-4-coordinated anions.

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TABLE 8. Hydrogen bonding in hejtmanite.

D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	∠ DHA (°)
X^{O}_{A}(1)OH–H(1)…O(5)a	0.98(1)	2.48(3)	3.285(4)	140(3)
X^{O}_{A}(1)OH–H(1)…O(9)a	0.98(1)	2.59(3)	3.339(4)	133(3)
X^{O}_{A}(2)OH–H(2)…O(11)b	0.98(1)	2.31(3)	2.931(3)	120(3)
X^{O}_{A}(2)OH–H(2)…O(4)b	0.98(1)	2.43(3)	2.976(3)	115(3)

a: x-½, y-$^{1}/_{2}$, z; b: -x+1, -y+1, -z+1.

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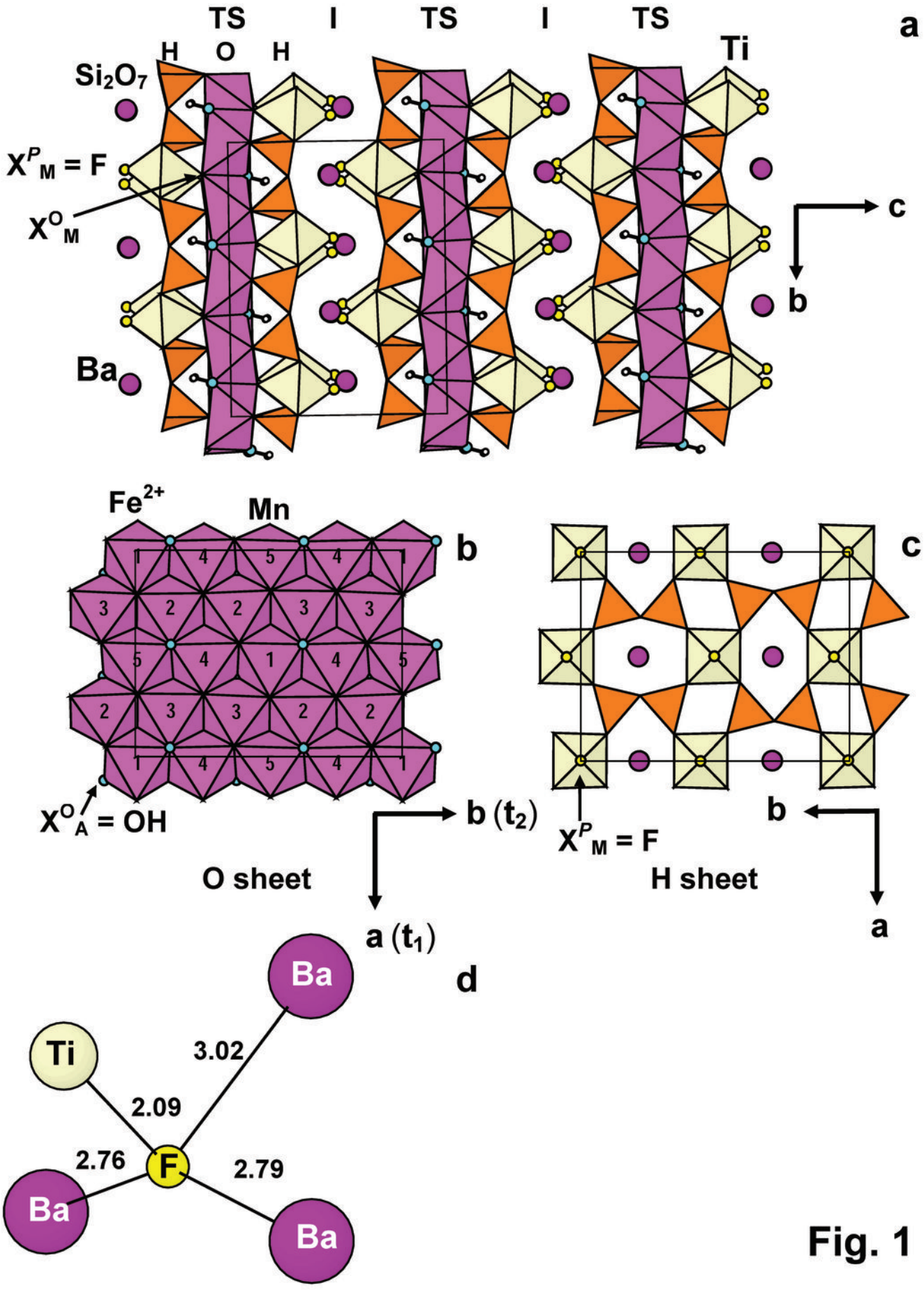

Fig. 1

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